CATALYTIC HYDROPYROLYSIS OF COAL
TO DISTILLATE OILS

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INTRODUCTION

Coal is predominantly aromatic in nature and deficient in hydrogen. It contains only about 4.5-5.0 percent hydrogen as compared to crude oils which contain 11-13 percent hydrogen. Coal therefore, can be converted to a crude oil type liquid either by removing carbon from it or by adding hydrogen to it. Pyrolysis processes come under the first category which produce large quantities of carbon rich char and small quantities of hydrogen rich tar. Under practical conditions of pyrolysis[1], tar yield varies between 20 and 25 percent with char yield of about 50 percent. Pyrolysis tars are poor in quality and require catalytic hydrotreatment for conversion to refined products.

The yield and quality of tar can be improved by carrying out coal pyrolysis under hydrogen pressure. In hydropyrolysis, hydrogen improves tar yield by stabilizing reactive fragments formed from coal during pyrolysis. In the absence of hydrogen, some of the reactive fragments undergo polymerization and condensation reactions forming char. Hydrogen also improves tar quality by promoting hydrocracking and hydrorefining of tar during the pyrolysis process. In most of the hydropyrolysis work,[2-8] light oils containing mostly BTX are produced in low yields of 10-20 percent. The hydropyrolysis processes operate at very high temperatures of 700-1000°C where the primary tar undergoes extensive hydrocracking forming BTX and gas.

The yield and quality of tar can be further improved by carrying out hydropyrolysis at medium temperatures of 500-600°C in the presence of a catalyst that promotes hydrogenation and hydrocracking reactions. Though work on pyrolysis[9] and hydropyrolysis[10] of coal was done extensively, very little is known about catalytic hydropyrolysis. Schroeder[11] patented a catalytic hydrogenation process where he claimed that a bituminous coal impregnated with ammonium molybdate yielded 30-60 percent light oil at 800°C and 2000 psi pressure. Friedman et al[12] hydrogenated a New Mexico coal impregnated with one percent molybdenum in the form of ammonium molybdate in fixed and fluid beds. Most of the experimental work was done at 600-900°C under a pressure of 6000 psi. Most of the coal was converted to gas with a liquid yield of less than 20 percent. But high yield of coal liquid of up to 57 percent was obtained when the hydrogenation was carried out at 480°C under a pressure of 6000 psi. Steinberg and Fallon[13] hydropyrolyzed a lignite impregnated with ammonium molybdate at 700°C and 1500 psi pressure in a free fall tubular reactor. The yield of liquid product was reported to be about 18-25 percent but the catalyst did not affect the conversion. Franklin et al[14] studied the effect of mineral matter on rapid pyrolysis and hydropyrolysis of a bituminous coal and found no significant effect by iron-sulfur minerals at a hydrogen pressure of about 1000 psi. In this paper, the results of catalytic hydropyrolysis of coal in a hanging basket reactor and a fluid bed reactor are described. Refined distillate oils are obtained from coal at medium temperatures and pressures in the presence of a hydrocracking catalyst.

EXPERIMENTAL

The experimental work was done in a Hanging Basket Reactor (HBR) system shown in Figure 1 and a Fluidized Bed Reactor system shown in Figure 2. The Hanging Basket Reactor consists of a high pressure vessel of 2" i.d. and 4' long provided with a heater at the bottom and a basket at the top. The basket hangs from a shaft connected to a valve and carries a crucible. The HBR was designed for a pressure of 7000 psi at a temperature of 500°C. Physical mixtures containing one gram of coal and three grams of catalyst were taken in the crucible and the system was pressurized and heated to the desired conditions. After the system conditions were stabilized, the crucible was lowered to the hot zone and kept there for different periods of time and then raised to the original position. The lowering and raising operations take 2-3 seconds. After this operation, the system was cooled, depressurized and the crucible was taken out of the system. The weight lost by coal during the reaction was taken as the conversion. Some experiments were also done with 50 and 100 grams of coal in a 1-litre Magnedrive Autoclave under simulated conditions of the HBR work to prepare bulk quantity of liquid product for analysis.

The Fluid Bed Reactor System was designed for a working pressure of 4000 psi at a maximum temperature of 700°C. It consists of a fluid bed reactor of 1.5" i.d. and 4' height, two hydrogen heaters, three coolers, two liquid collection bottles, a steam injection system, a flow control valve, a dry gas meter and a pump to circulate chilled water trough the coolers. The fluid bed reactor has a liner of 1.25" i.d. and 3.5' height which is provided with a perforated disc at the bottom to support the coal-catalyst mixture. The system is fully instrumented with controllers, indicators and recorders for temperature, pressure, Δp and gas flow. The reactor system was housed in a high pressure cell and operated from outside at the control panel.

The fluid bed reactor was operated in a batch mode with hydrogen flowing through it continuously. A physical mixture of coal and catalyst was placed in the liner which was then introduced into the reactor. The size of coal and catalyst and fluidization velocity were predetermined using a glass fluid bed reactor at ambient temperature. Fluidization studies with coal-catalyst mixtures showed that coal and catalyst particles of 35-150 mesh fluidize well with good mixing at velocities of 0.25 to 0.5 ft./sec. which give gas phase residence times of 6-12 seconds for a coal-catalyst fluid bed height of 3'. After the introduction of the liner into the reactor, the system was flushed with nitrogen, pressurized and closed to the atmosphere. The hydrogen heaters were heated to the desired temperature and the nitrogen in the system was replaced by hydrogen through a bypass line. Flow of hydrogen through the bypass was continued until the desired gas flow and temperature were attained. At that stage, the hot hydrogen flow was diverted through the reactor where it came into contact with the coal and catalyst and fluidized the mixture. The reaction was carried out for 10 to 30 minutes. At the end of the reaction period, the hydrogen flow was diverted back through the bypass and was replaced by nitrogen. During the operation, chilled water was circulated through the coolers. The liquid product was condensed in the coolers and was collected in the collection bottles. The gas was let out into the atmosphere through the gas meter where its volume was recorded. The solid char remained in the liner with the catalyst.

A bituminous coal from Utah was used in the HBR work. The analysis of the coal is given in Table 1. A Wyoming subbituminous and a Kentucky bituminous coal were used in the FBR work. The analysis of the coals is given in Table 2.

Prereduced tungsten disulfide (WS_2) of -200 mesh size was used in the HBR experiments. A commercial catalyst containing sulfides of cobalt and molybdenum supported on silica-alumina was used in the FBR experiments. The catalyst was ground to 60-140 mesh size before use. The analyses of coals, coal liquids and gases were done by standard methods.

RESULTS AND DISCUSSION

The Hanging Basket Reactor experiments were done with and without the catalyst at 450-550°C under a pressure of 2000-4000 psi. The effect of reaction time and temperature on coal conversion is shown in Figure 3. The conversion increased with temperature and time. In the case of non-catalytic experiments, a maximum conversion of 43 percent was obtained at 550°C and 4000 psi pressure. The addition of catalyst increased the conversion significantly. Coal conversion of over 90 percent was obtained at 550°C and 4000 psi pressure. The data show that adequate catalytic effect can be obtained in coal conversion when coal and catalyst are present in a physical mixture at high temperatures, high pressures and high catalyst-coal ratios. The data also show that high coal conversions can be obtained in catalytic hydropyrolysis at short reaction times of less than 10 minutes.

The effect of hydrogen pressure and reaction time on coal conversion at 550°C is shown in Figure 4. Hydrogen presure did not affect the non-catalytic conversion but increased the catalytic conversion significantly. It was reported in the earlier publications[7,15] that hydrogen pressure increased conversion in the non-catalytic hydropyrolysis of coal. But most of the published work was carried out at lower pressures and thus can not be compared with the data obtained in the present work. It is therefore concluded from the data of Figure 4 that hydrogen pressure increases coal conversion in non-catalytic hydropyrolysis only at pressures lower than 2000 psi but it does not affect the conversion at pressures of 2000 psi or higher unless a catalyst is present. The pressure effect in catalytic hydropyrolysis appears to be similar to the effect observed in catalytic hydrogenation of coal.[16,17]

Significant differences were observed in the nature of liquid and gaseous products obtained in the HBR work. Table 3 contains the analysis of liquid and gaseous products. The product obtained in the non-catalytic work was a very high boiling liquid and contained large quantities of preasphaltene, asphaltene, sulfur and nitrogen. On the other hand, the catalytic product was lighter and contained substantial amounts of light and middle oils. The preasphaltene, asphaltene, sulfur and nitrogen content of the product was very low. The properties of the catalytic liquid product indicate that the primary liquid formed from coal underwent hydrorefining and hydrocracking in the presence of the catalyst yielding a refined distillable oil. The data suggest that in catalytic hydropyrolysis the conversion of coal to liquid product takes place by a two step reaction mechanism shown in Figure 5. In pyrolysis, the organic matter of coal undergoes thermal breakdown forming an intermediate product consisting of reactive fragments. Some of the fragmented coal molecules undergo stabilization forming tar and some of the fragments undergo polymerization and condensation reactions forming coke or char. In hydropyrolysis, hydrogen reacts with the fragmented coal molecules and stabilize them before they undergo polymerization and condensation reactions which lead to coke or char formation. Tar yield therefore increases in hydropyrolysis when compared to just pyrolysis of coal. In catalytic hydropyrolysis, the primary coal liquid appears to be forming due to pyrolysis and catalytic hydrogenation of coal The primary coal liquid in turn undergoes catalytic hydrocracking forming a lighter liquid product.

It is concluded from the foregoing discussion on catalytic hydropyrolysis that physical contact between coal and a solid catalyst provides adequate catalytic effect to get high coal conversion of up to 90 percent. The coal undergoes liquefaction and the liquefied coal undergoes refinement in a single step, thus producing good quality light and middle oils. Though not discussed in this paper, catalyst to coal ratios of 3 to 1 were found to provide adequate catalytic effect and to reduce agglomeration of caking coals when the size of coal was >200 mesh. It is therefore feasible to produce refined distillate oils in high yields from caking bituminous coals in a single step by catalytic hydropyrolysis under the conditions used in the HBR work. The HBR system does not have any potential for use as a practical system to liquefy coal on a large scale in a continuous manner. An evaluation of several practical reactor systems led to the conclusion that a fluidized bed reactor is the most suitable for this application.

The results of the Fluidized Bed Reactor System are given in Tables 4-6. Table 4 contains the test conditions used in the FBR work. The size of coal and catalyst and fluidization velocity were determined from fluidization studies made in a glass fluid bed reactor at ambient temperature and atmospheric pressure with nitrogen as the fluidizing gas. The temperature and pressure were selected from the HBR work. Table 5 contains the material balance of FBR work. The yield of liquid product from the subbituminous coal was about 33 percent as compared to about 43 percent from the bituminous coal. The hydrogen consumption was 2.5 and 3.8 percent respectively. It is conceivable that the liquid product yield can be improved under optimal processing conditions. Table 6 contains the properties of liquid products. The coal liquids contain small amounts of sulfur and benzene insolubles and large quantities of light and middle oils. The liquid from the subbituminous coal contains 75 percent distillate and the liquid from the bituminous coal contains 86 percent distillate boiling up to a temperature of 450°C. The data indicate that coal liquefaction and refining of liquefied coal took place in a single step in the FBR which is in conformity with the HBR data. The data also support the two step reaction mechanism shown in Figure 5.

ACKNOWLEDGMENT

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Table 1. Analysis of Utah Coal

Proximate Analysis, Wt.% (Dry basis)		
Volatiles	:	46.8
Fixed Carbon	:	46.5
Ash	:	6.7
Ultimate Analysis, Wt.% (Dry basis)		
Carbon	:	81.22
Hydrogen	:	5.98
Nitrogen	:	1.61
Sulfur	:	2.41
Oxygen (By difference)	:	9.18

Table 2. Analysis of Coals

Proximate Analysis, Wt.% (Dry basis)		Subbituminous Coal (Wyoming)	Bituminous Coal (Kentucky #6 and #11)
Volatiles	:	43.22	46.43
Fixed Carbon	:	50.55	44.17
Ash	:	6.23	9.40
Ultimate Analysis, Wt.% (Dry basis)			
Carbon	:	70.21	73.44
Hydrogen	:	4.94	5.30
Nitrogen	:	1.05	1.21
Sulfur	:	0.71	3.35
Oxygen (By difference)	:	16.86	7.30

Table 3. Analysis of HBR Products

Reaction Conditions

Temperature	:	550°C
Pressure	:	400 psi
Reaction time	:	10 minutes

Liquid product		Catalytic	Non-Catalytic
Sp. gr. at 25°C	:	0.9915	-
Sulfur, Wt.%	:	0.42	1.24
Nitrogen, Wt.%	:	0.68	1.34
Light oil, Wt.% (-200°C)	:	18.0	3.0
Middle distillate, Wt.% (200-450°C)	:	72.0	28.0
Heavy liquid, Wt.% (+450°C)	:	10.0	69.0
Gaseous product			
Methane, Vol.%	:	11.0	28.0
Ethane, Vol.%	:	24.0	40.0
Propane, Vol.%	:	36.0	17.0
Butanes, Vol.%	:	29.0	15.0

Table 4. FBR Test Conditions

Wt. of coal in each test, g	:	130
Wt. of catalyst in each test, g	:	145
Size of coal, Tyler mesh	:	35-60
Size of catalyst, Tyler mesh	:	60-140
Fluidization velocity, ft./sec.	:	0.45
Temperature, °C	:	550
Pressure, PSI	:	2000
Reaction time, min.	:	20

Table 5. FBR Material Balance (daf Coal)

		Subbituminous Coal	Bituminous Coal
Input, g.			
Coal	:	100.0	100.0
Hydrogen	:	2.5	3.8
TOTAL		102.5	103.8
Output, g.			
Liquid	:	32.6	42.7
Gas (Includes H_2S and NH_3)	:	12.3	17.0
Water	:	3.5	5.3
Solid	:	54.1	38.8

Table 6. Analysis of FBR Liquid Product

		Subbituminous Coal	Bituminous Coal
Sp. gr., 25°C	:	1.02	1.04
Sulfur, Wt.%	:	0.38	0.41
Nitrogen, Wt.%	:	1.04	1.11
Light oil, Wt.% (-200°C)	:	15.0	17.0
Middle distillate, Wt.% (200-450°C)	:	60.0	69.0
Benzene insolubles, Wt.%	:	9.1	6.1

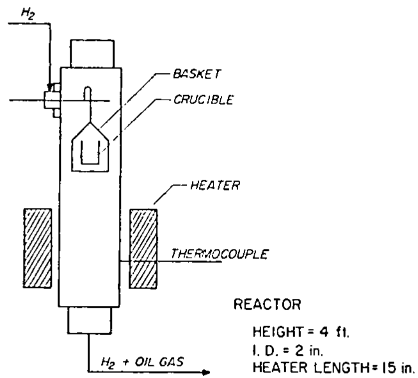

FIGURE 1. HANGING BASKET REACTOR SYSTEM

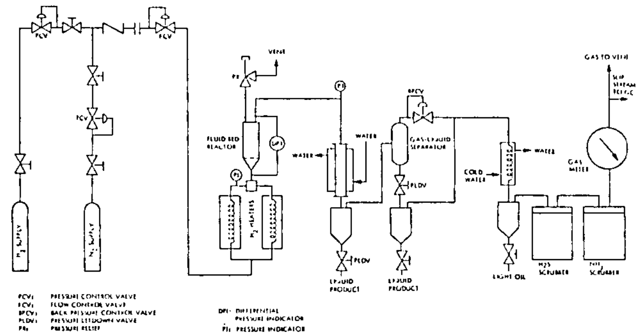

FIGURE 2. FLUID BED REACTOR SYSTEM

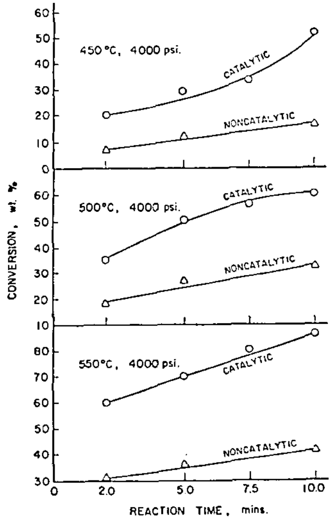

FIGURE 3. EFFECT OF TEMPERATURE AND REACTION TIME ON CONVERSION

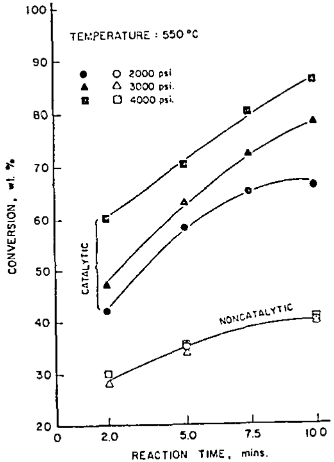

FIGURE 4. EFFECT OF PRESSURE AND REACTION TIME ON CONVERSION

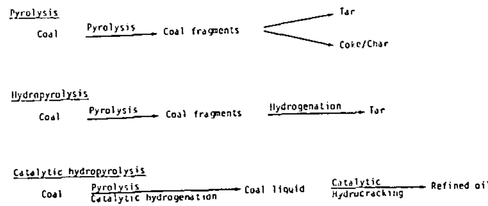

FIGURE 5. MECHANISM OF CATALYTIC HYDROPYROLYSIS